On the Interfacial Rate of Reaction of CO_2 with a Calcium Ferrite Melt

S. SUN, Y. SASAKI, and G. R. BELTON

Measurements of the rate of dissociation of CO_2 have been made by the $^{14}CO_2$-CO isotope exchange technique on calcium ferrite melts with Ca/Fe = 0.30 at 1300 °C. Studies have also been made of the interfacial rates of oxidation of calcium ferrite melts with an average CaO content of 19.45 wt pct (Ca/Fe $\simeq$ 0.33) in CO_2-CO atmospheres at 1362 °C. It is shown that the rates of oxidation are consistent with the rates of isotope exchange, indicating a common rate determining step. Measurements of the equilibrium Fe^{3+}/Fe^{2+} ratio as a function of the CO_2/CO ratio for 19.3 wt pct CaO melts at 1360 °C and for 28.7 and 18.6 wt pct CaO melts at 1300 °C are found to be in close agreement with the deductions of Takeda, Nakazawa, and Yazawa. Combination of the equilibrium data with the results of the isotope exchange studies indicate that the apparent first order rate constant for the dissociation of CO_2 is inversely proportional to the square of the Fe^{3+}/Fe^{2+} ratio of the melt, as has been previously found for liquid iron oxide, lime-saturated calcium ferrites, silica-saturated iron silicates, and an equimolar "FeO"-CaO-SiO_2 melt.

I. INTRODUCTION

RECENT studies by isotope exchange techniques[1,2] of the rate of dissociation of CO_2 on some FeO- and MnO-containing oxide melts have shown that the apparent first order rate constant for each melt, k_a, is a function of the state of oxidation of the melt as well as temperature. For liquid "FeO" at 1420 and 1500 °C, "FeO"-CaO(sat) at 1230, 1500, and 1550 °C, "FeO"-SiO_2(sat) at 1240 and 1400 °C, and MnO-SiO_2(sat) at 1500 °C, k_a was found to be inversely proportional to the activity of oxygen, a_O, in the melt over the ranges of conditions which were studied. For the above iron oxide-containing melts, available thermodynamic data[3–6] are closely consistent with the relationship:

$$(Fe^{3+}/Fe^{2+})^2 \propto a_O \qquad [1]$$

for each system. Accordingly, forward rates of reaction may be written in the form:

$$v = k_a p\mathrm{CO}_2 = k_a^\circ p\mathrm{CO}_2 a_O^{-1} \qquad [2]$$

or

$$v = kp\mathrm{CO}_2(Fe^{3+}/Fe^{2+})^{-2} \qquad [3]$$

where a_O may be conveniently defined as the CO_2/CO ratio which would be in equilibrium with the melt, and k_a° and k are system and temperature dependent constants.

The simple inverse dependence on the activity of oxygen was found *not* to hold for the equimolar "FeO"-CaO-SiO_2 melt and, possibly, for some other unsaturated melts.[2] For the equimolar melt at 1420 °C, forward rates were described by the expression:

$$v = k_a^\circ p\mathrm{CO}_2 a_O^{-0.75(\pm 0.06)} \qquad [4]$$

over the accessible experimental conditions. However, the equilibrium results of Timucin and Morris[7] were shown to be reasonably consistent with the relationship:

$$Fe^{3+}/Fe^{2+} \propto a_O^{0.4} \qquad [5]$$

for the equimolar melt over the conditions of temperature and oxygen activity of the kinetic studies. Accordingly, it was concluded that the kinetic data were still in accord with the rate law [3]. This is illustrated in Figure 1, where apparent first order rate constants (mol cm^{-2} s^{-1} atm^{-1}) for several of the melts are presented logarithmically as a function of the Fe^{3+}/Fe^{2+} ratio, and where the lines are drawn with a slope of −2.

The present isotope exchange studies on a nominal "FeO"-20 wt pct CaO melt at 1573 K were undertaken to examine in more detail the dependence of the apparent first order rate constant on the Fe^{3+}/Fe^{2+} ratio for a melt which has a

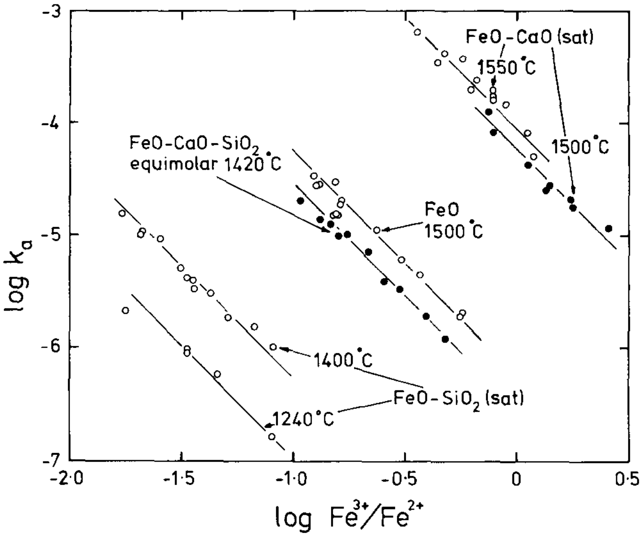

Fig. 1 — Apparent first order rate constants (mol cm^{-2} s^{-1} atm^{-1}) for the dissociation of CO_2 as a function of the Fe^{3+}/Fe^{2+} ratio for iron oxide-containing melts.[1,2] Lines are drawn with a slope of −2.

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Manuscript submitted January 7, 1988.

well-established deviation from the "ideal" behavior represented by Eq. [1]. An "FeO"-CaO melt was chosen for this purpose in view of the deductions by Takeda *et al.*[5] from their own and other work[3,4,7,8] that equilibrium Fe^{3+}/Fe^{2+} ratios were closely described by the expression:

$$\log(Fe^{3+}/Fe^{2+}) = 0.170 \log pO_2 + 0.018 \text{ (wt pct CaO)} + \frac{5500}{T} - 2.52 \qquad [6]$$

for "FeO"-CaO melts containing 10 to 35 wt pct CaO from about 1473 to 1873 K and for values of pO_2 between about one order of magnitude above that for iron saturation to 10^{-4} atm.

Recent work by Hara *et al.*,[9] however, is consistent with a higher dependence for the equilibrium Fe^{3+}/Fe^{2+} ratio on pO_2. For the "FeO"-20 wt pct CaO melt at 1773 K and with values of pO_2 between about 10^{-6} and 0.2 atm, they obtained:

$$\log(Fe^{3+}/Fe^{2+}) = 0.208 \log pO_2 + 1.049 \qquad [7]$$

Accordingly, additional measurements have been made of the equilibrium Fe^{3+}/Fe^{2+} ratio as a function of the CO_2/CO ratio to confirm the dependence over the range of conditions of the isotope exchange experiments.

Rate constants for the reduction of liquid "FeO" and "FeO"-SiO_2 melts[10,11] and an iron oxide-containing slag[12] at iron saturation in CO-containing atmospheres have been shown[1,2,13] to be in close accord with rate constants for the isotope exchange reaction. It was concluded that the rate determining interfacial chemical step in the oxidation and reduction of these melts in CO_2- and CO-containing atmospheres must be that for the dissociation and formation of CO_2. A similar conclusion was tentatively reached in the case of "FeO"-CaO melts in view of the agreement between the extrapolated value of the rate constant for isotope exchange on the CaO-saturated melt and reported values[14] of the rate constant for the oxidation of liquid calcium ferrites in CO_2-CO atmospheres at 1550 °C. This has been investigated further in the present work by measurement of the rates of reaction of CO_2-CO mixtures with "FeO"-20 wt pct CaO melts at an average temperature of 1635 K.

II. EXPERIMENTAL DETAILS

A. *Isotope Exchange Studies*

The experimental technique was essentially the same as that described in previous papers.[1,2] Mixtures of ^{14}C enriched CO_2 and natural CO were passed down a 3 mm ID alumina tube to within about 5 mm of the surface of about 0.5 gm of the melt held at the base of an open-ended refractory containment tube (7 to 11 mm ID) which was inserted into a shallow well in an inductively heated platinum-rhodium susceptor. Temperature measurement was by means of a noble metal thermocouple inserted into the base of the susceptor and the whole assembly was held within a silica reaction tube by O-ring sealed end caps. After about 30 minutes, the exiting gas mixture was stripped of CO_2 by passing through a molecular sieve (Linde 13X) and Ascarite, and the resulting CO was converted to CO_2 by passing through CuO granules at about 300 °C. Counting of the ^{14}C contents of samples of the resulting and initial O_2 was by the previously described[15] internal Geiger-Müller tube method.

A master slag was prepared by melting reagent grade Fe_2O_3 and CaO in a heavy iron crucible and quenching on a steel plate. Chemical analysis of the slag gave a molar ratio of Ca to Fe of 0.30 with major impurities of 0.40 wt pct SiO_2, 0.10 wt pct P_2O_5, and 0.04 wt pct Al_2O_3. In order to minimize changes in slag composition through absorption of iron into the Pt-Rh susceptor at low values of the CO_2/CO ratio, the susceptor was usually preconditioned in preliminary experiments with samples of the master slag under the CO_2/CO ratio of interest.

B. *Equilibrium and Oxidation Rate Studies*

Samples of the slag (0.10 g) were held in a squat platinum crucible (9 mm ID × 10 mm) suspended by a platinum wire which passed through an impervious mullite gas inlet tube (3 mm ID) held vertically within the alumina reaction tube of a molybdenum or platinum-rhodium wound resistance furnace by an appropriate system of O-ring sealed end caps. A noble metal thermocouple was attached near to the tip of the gas inlet tube. A CO_2-CO mixture of the desired ratio was passed for about 20 minutes to flush out the reaction tube and then the crucible was slowly raised until the gas inlet tube was within the mouth of the crucible, *i.e.*, about 8 mm from the surface of the melt. After a further period of at least 10 minutes, the crucible was either dropped to a water cooled brass block at the bottom of the reaction tube or held under a second CO_2-CO mixture for a measured reaction time before being dropped. The quenched crucible and contents were weighed and placed in oxygen-free hydrochloric acid saturated with flowing CO_2. After dissolution of the slag, aliquots of the solution were titrated for ferrous and total iron with standardized potassium dichromate solution. The crucible was then rinsed, dried, and reweighed.

Most experiments were carried out with the master slag which had been prepared for the isotope exchange experiments. Additional slags were prepared by melting together A.R. grade Fe_2O_3 and CaO in a platinum crucible. Gases were purified by standard methods[16] and flowrates were measured by calibrated capillary flowmeters. Two complete gas trains were used to allow a rapid, essentially single action changeover in CO_2/CO ratio for the reaction rate studies.

III. RESULTS

A. *Rates of Dissociation of CO_2*

As discussed earlier,[1] the isotope exchange between CO_2 and CO may be assumed to involve the dissociation and reforming of molecules of CO_2 at the surface of the melt. The apparent rate constant for the dissociation of CO_2, first order with respect to pCO_2, is given by:[1]

$$k_a = \frac{\dot{V}}{ART} \frac{1}{1 + B} \ln\left[\frac{1}{1 - N(1 + B)/N'B}\right] \qquad [8]$$

where $\dot{V}$ is the total volume flowrate of the gas mixture, A is the surface area of the melt, B is the value of the CO_2/CO ratio, and N' and N are the relative concentrations of ^{14}C (counting rates) in the ingoing CO_2 and in the CO_2 which results from the conversion of CO to CO_2 after the reaction, respectively.

In these studies, values of N' ranged between 5000 and 30,000 min^{-1} and values of N were between 100 and 2000 min^{-1} above a background count of about 300 min^{-1} for natural CO_2. Flowrates were in the range 185 to 450 ml min^{-1} (STP) and nominal melt areas were 0.38 to 0.95 cm^2. The results for the experiments at 1300 °C with recrystallized alumina, sapphire (single crystal alumina), and lime-stabilized zirconia containment tubes are presented logarithmically in Figure 2 as values of the apparent first order rate constant, k_a, in units of mol cm^{-2} s^{-1} atm^{-1}, *vs* the value of the imposed CO_2/CO ratio. Clearly, there is no significant effect of type of containment tube on the results.

The best straight line shown drawn through the data is given by the expression:

$$k_a = 2.88(\pm 0.28) \times 10^{-5}(pCO_2/pCO)^{-0.79(\pm 0.06)} \cdot \text{mol cm}^{-2}\ \text{s}^{-1}\ \text{atm}^{-1} \qquad [9]$$

where the uncertainties represent two standard deviations.

Detailed chemical analyses of iron and calcium oxide contents were not carried out on all the slag films subsequent to these experiments but, in view of the preconditioning of the susceptor and the low absorptions of iron into the platinum crucibles during the oxidation and equilibrium experiments (noted later), the above equation is taken to represent the rate constants for a melt with constant molar ratio Ca/Fe = 0.3. Some contamination of the melts occurred through reaction with the containment tubes. Al_2O_3 contents of solidified slag films were found to be in the range 5 to 9 wt pct when recrystallized alumina or sapphire containment tubes were used. ZrO_2 contents were in the range 10 to 15 wt pct when stabilized zirconia was used. In the latter case, however, scanning electron microscopy showed the presence of jagged particles of zirconia-rich material in the solidified films, presumably from degradation of the fragile knife edge of the containment tube. EDAX measurements of particle-free areas of the film gave ZrO_2 contents of 4 to 11 wt pct, but predominantly in the range 4 to 6 wt pct.

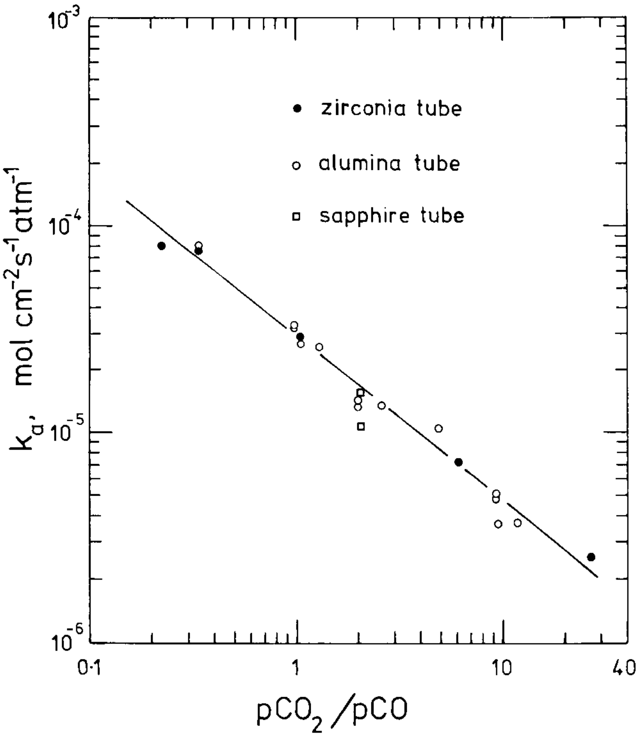

Fig. 2 — Apparent first order rate constants for the dissociation of CO_2 on a calcium ferrite melt with Ca/Fe = 0.3 at 1300 °C as a function of the equilibrium CO_2/CO ratio from the isotope exchange measurements.

B. *Equilibrium Results*

Ferric and ferrous oxide contents were determined for melts produced from samples of the master slag equilibrated with CO_2/CO ratios between 0.25 and 140 at a temperature of 1360 (±7) °C. The average total iron oxide content, which showed no significant trend with the CO_2/CO ratio, was 80.2 wt pct with an average scatter of about 0.7 wt pct. Assuming that the impurity content remained constant at 0.5 wt pct, the results, which are presented in Figure 3, are taken to be those for a melt with an average CaO content of 19.3 wt pct at a temperature of 1360 °C.

The best straight line through all the data, shown as the dashed line in Figure 3, is given by the expression:

$$\log(Fe^{3+}/Fe^{2+} = -0.36(\pm 0.02) + 0.36(\pm 0.02)\log(pCO_2/pCO) \qquad [10]$$

where the uncertainties represent two standard deviations. Combination of Eq. [6], from the work of Takeda *et al.*,[5] with thermodynamic data[17] for the reaction

$$2CO_2 = 2CO + O_2 \qquad [11]$$

gives the expression:

$$\log(Fe^{3+}/Fe^{2+}) = 0.34\log(pCO_2/pCO) + 0.018(\text{wt pct CaO}) + 480/T - 0.98 \qquad [12]$$

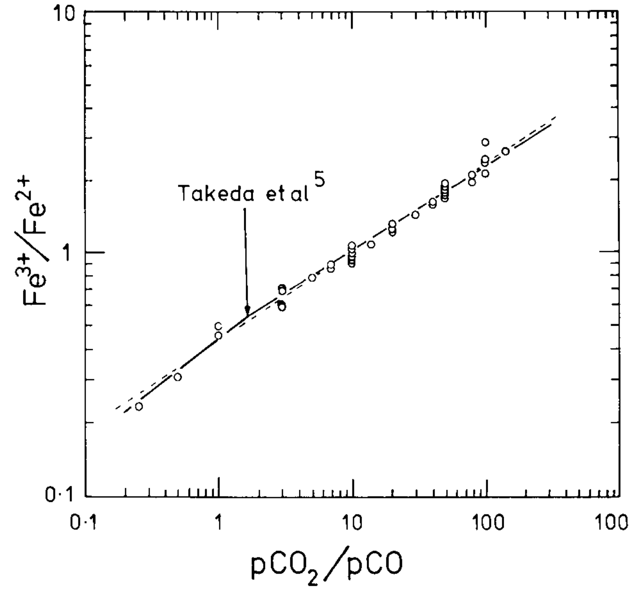

Fig. 3 — Equilibrium Fe^{3+}/Fe^{2+} ratios as a function of the CO_2/CO ratio for a calcium ferrite melt with an average CaO content of 19.3 wt pct at 1360 °C, in comparison with the work of Takeda *et al.*[5]

valid for pCO_2/pCO above about 2. Values derived from this equation are in close accord with the present experimental results, as is illustrated by the continuous line in Figure 3. The trend of the results at CO_2/CO ratios below 2 also appears to be fully consistent with the work of Takeda *et al.* The results of less extensive measurements at 1300 °C on melts with mean CaO contents of 28.7 and 18.6 wt pct are presented in Figure 4. Again, the results are in close agreement with the work of Takeda *et al.*[5]

C. *Rates of Oxidation in CO_2-CO Mixtures*

Six sets of oxidation experiments were carried out on the nominally 20 wt pct CaO melt. Values of the CO_2/CO ratio in the pre-equilibration and oxidizing gas mixtures were, respectively, 3 and 6, 7 and 14, 10 and 20, 20 and 50, 30 and 50, and 40 and 80. The mean temperature was 1362 ±6 °C and the mean iron oxide content ($FeO + Fe_2O_3$) of the quenched specimens was 80.05 ±0.48 wt pct. No significant trend in the total iron oxide content with oxidizing conditions was observed and, assuming that the impurity content remained constant at 0.5 wt pct, the experimental data are taken to be those for a melt with an average CaO content of 19.45 wt pct. Weight increases of the platinum crucibles were below 1 mg and predominantly below 0.5 mg. Since such weight increases were also typical of the equilibrium experiments over a similar range of CO_2/CO ratios, it is unlikely that the results were seriously affected by transfer of iron from the crucibles during the short periods of oxidation.

The results of the experiments are presented in Figures 5 and 6 in the form of wt pct Fe_2O_3 *vs* time. Zero time was assumed to be 2 seconds after the change-over in gas mixture since the volume of the glass and refractory tubes between the change-over stopcock and the surface of the melt was roughly 10 ml and a gas flowrate of 300 ml min^{-1} was used. Initial Fe_2O_3 concentrations for the pre-equilibration conditions were calculated from Eq. [12] for the average CaO content of 19.45 wt pct. These are shown as the short horizontal lines on the left-hand axes of Figures 5 and 6.

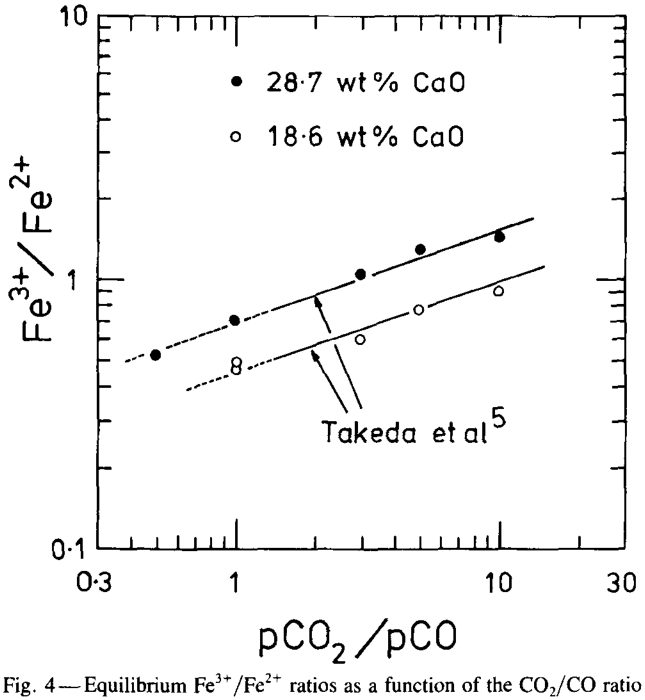

Fig. 4—Equilibrium Fe^{3+}/Fe^{2+} ratios as a function of the CO_2/CO ratio for two calcium ferrite melts at 1300 °C, in comparison with the work of Takeda *et al.*[5]

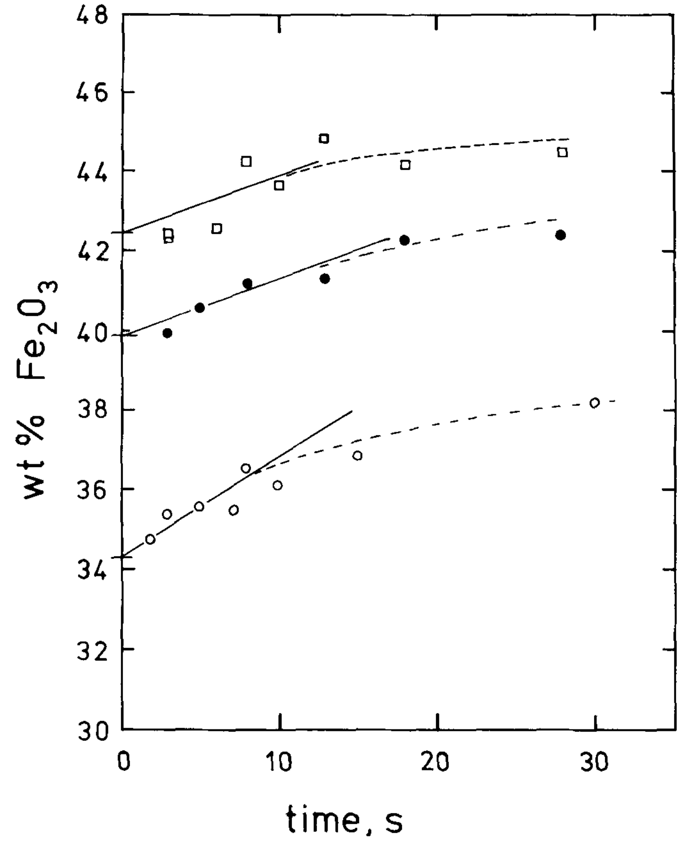

Fig. 5—Fe_2O_3 content *vs* time for the oxidation of calcium ferrite melts with an average CaO content of 19.45 wt pct at 1362 °C. CO_2/CO ratios in the gas mixture for pre-equilibration and oxidation were, respectively, ○, 3 and 6; ●, 7 and 14; □, 10 and 20.

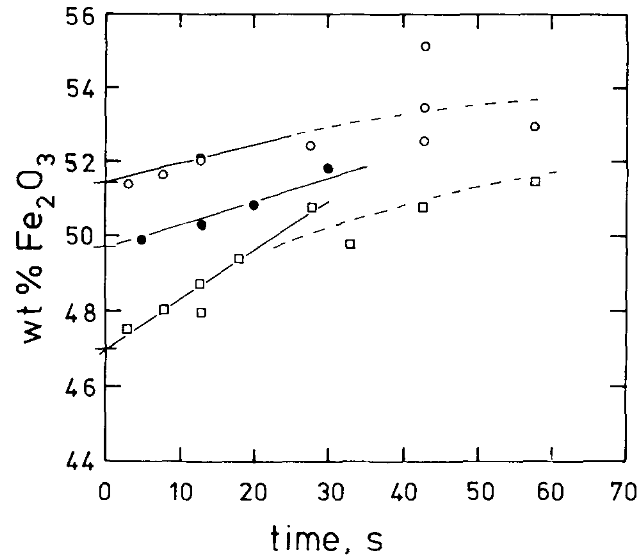

Fig. 6—Fe_2O_3 content *vs* time for the oxidation of calcium ferrite melts with an average CaO content of 19.45 wt pct at 1362 °C. CO_2/CO ratios in the gas mixture for pre-equilibration and oxidation were, respectively, □, 20 and 50; ●, 30 and 50; ○, 40 and 80.

The rate of reaction, v, in mol cm^{-2} s^{-1}, is given by:

$$v = \frac{W}{16{,}000A}\frac{d\,\text{pct Fe}_2\text{O}_3}{dt} \qquad [13]$$

where W is the mass of the melt (g) and A is the exposed surface area (cm^2). Rates, derived from the slopes drawn in Figures 5 and 6, are listed in Table I.

Assuming that the reaction is first order with respect to $p\text{CO}_2$ leads to the rate law:

$$v = k_a[p\text{CO}_2 - (p\text{CO}_2)_e] \qquad [14]$$

where $(p\text{CO}_2)_e$ is the partial pressure of CO_2 which would be in equilibrium with the melt and the pressure of CO in the oxidizing atmosphere. Taking this latter pressure to be that in the exiting gas mixture, *i.e.*, corrected for the rate of production of CO, and assuming that the rates refer to average melt compositions at about the mid-points the linear regions in Figures 5 and 6, leads to the values of the apparent first order rate constant shown in the last column of Table I. Assuming an uncertainty of ±0.4 wt pct in the initial Fe_2O_3 contents and drawing several initial slopes through the experimental data suggests that these values are uncertain by a factor of about 2.

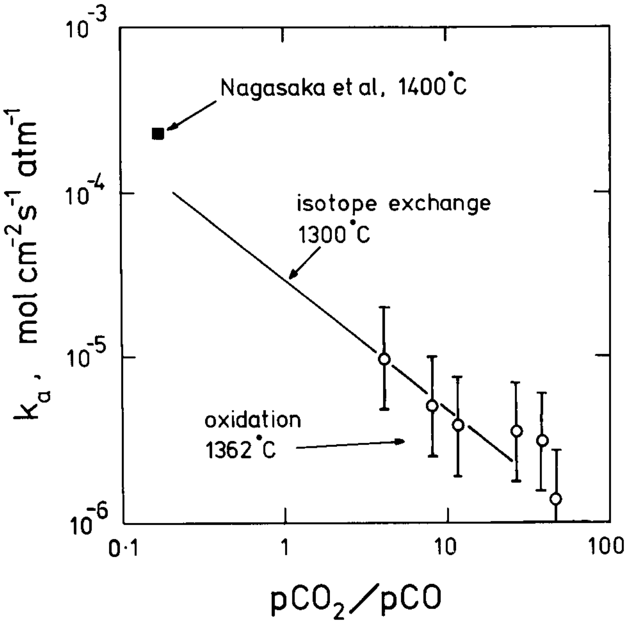

Fig. 7 — Apparent first order rate constants for the oxidation of calcium ferrite melts by CO_2 as a function of the oxygen activity of the melt expressed as the equilibrium CO_2/CO ratio. Ca/Fe = 0.3.

IV. DISCUSSION

A. *Rates of Reduction, Oxidation, and Isotope Exchange*

Nagasaka *et al.*[10] have measured rates of reduction of calcium ferrite melts at iron-saturation in CO-containing atmospheres. Under conditions where the effects of mass transfer processes could be ignored, the rates were found to be first order with respect to the pressure of CO, *i.e.*,

$$v = k'p\text{CO} \qquad [15]$$

The interpolated value of k' for the 24 mol pct CaO melt (Ca/Fe = 0.3) at 1400 °C is 3.9×10^{-5} mol cm^{-2} s^{-1} atm^{-1}.

From Takeda *et al.*,[5] iron saturation for this melt at 1400 °C occurs at $p\text{CO}_2/p\text{CO} = 0.17$. Accordingly, and assuming microscopic reversibility, the first order rate constant for oxidation of this melt, k_a, should be about 2.3×10^{-4} mol cm^{-2} s^{-1} atm^{-1}. This value is shown to be in reasonable accord with the apparent first order rate constant for isotope exchange for the melt with a similar Ca/Fe ratio at 1300 °C in Figure 7. The difference would be fully accounted for by an activation energy of about 30 kcal mol^{-1} (125 kJ mol^{-1}).

Rate constants for the oxidation of melts at 1362 °C from the present work are also presented in Figure 7 as a function of the oxygen activity, expressed as the CO_2/CO ratio which would be in equilibrium with each melt. The Ca/Fe ratio for these melts is 0.33 ±0.01. Despite the temperature difference and the large uncertainties in the values, the trend and results are sufficiently close to those for the isotope exchange reaction to indicate that the rate determining steps are the same.

Thus, based on Eq. [9], the interfacial rate of oxidation (or reduction) of a calcium ferrite melt with Ca/Fe ≃0.3 in CO_2-CO atmospheres at 1300 °C should be described by the expression:

$$v = 2.88 \times 10^{-5}(p\text{CO}_2 a_\text{O}^{-0.79} - p\text{CO}a_\text{O}^{0.21})\text{mol cm}^{-2}\text{ s}^{-1} \qquad [16]$$

within an uncertainty of about ±20 pct, for values of a_O between about 0.2 (iron saturation) and 30.

B. *The Dependence of the Rate Constant on the State of Oxidation of the Melt*

In Figure 8, the apparent first order rate constants from the isotope exchange experiments are shown plotted logarithmically against the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio which would be in equilibrium with each value of the CO_2/CO ratio for a cal-

Table I. Initial Rates of Oxidation of Calcium Ferrite Melts Containing 19.45 Wt Pct CaO at 1362 °C in CO_2-CO Atmospheres

$p\text{CO}_2/p\text{CO}$		Rate	Ascribed Melt Composition	Rate Constant
Pre-equilibration	Oxidizing	mol cm^{-2} s^{-1} × 10^7	Wt Pct Fe_2O_3	mol cm^{-2} s^{-1} atm^{-1} × 10^6
3	7	24.4	35.8	9.8
7	14	13.7	41.0	4.5
10	20	13.7	43.1	3.9
20	50	12.7	48.9	3.5
30	50	6.0	51.0	3.0
40	80	4.9	52.0	1.3

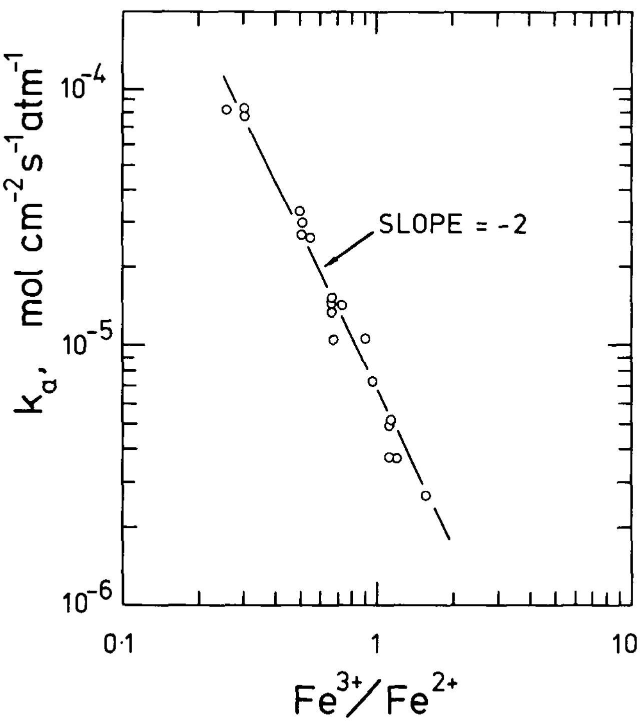

Fig. 8 — Apparent first order rate constants for the dissociation of CO_2 on a calcium ferrite melt with Ca/Fe = 0.3 at 1300 °C from the isotope exchange measurements, as a function of the Fe^{3+}/Fe^{2+} ratio of the melt.

cium ferrite melt with Ca/Fe = 0.3 at 1360 °C. In view of the agreement between the present equilibrium studies and the work of Takeda *et al.*,[5] the assessment of these latter workers was used to derive values of the Fe^{3+}/Fe^{2+} ratio. A slope of −2 is in good accord with the data.

As noted earlier, the melts contained Al_2O_3 or ZrO_2 from reaction with the containment tubes. Limited information obtained during phase equilibrium studies of the $FeO\text{-}Fe_2O_3\text{-}CaO\text{-}Al_2O_3$ system by Imlach and Glasser[18] is consistent with additions of several wt pct Al_2O_3 having negligible effect on the Fe^{3+}/Fe^{2+} ratio at low oxygen pressures. No information is available on the effect of ZrO_2 on equilibrium Fe^{3+}/Fe^{2+} ratios but, by analogy with the effect of TiO_2 on liquid iron oxide at iron saturation,[8] the effect is likely to be negligible. Accordingly, it is reasonable to conclude that the kinetic data are consistent with the relationship:

$$k_a \propto (Fe^{3+}/Fe^{2+})^{-2} \qquad [17]$$

over the range of conditions of the experiments.

From the present work and the data summarized in Figure 1 it thus appears that for liquid iron oxide and melts of high iron oxide concentration containing silica and/or lime, expression [17] describes the dependence of the apparent first order rate constant on the state of oxidation of each melt — at least over the range of conditions accessible to the isotope exchange technique.

As previously discussed,[1,2] expression [17] and rate law [3] are consistent with a predominant rate determining step which involves the dissociation of a doubly charged (negative) adsorbed CO_2 molecule or activated complex which includes one CO_2 molecule. The surface concentration of the transient charged species is given in terms of pCO_2 and the *concentrations* of electron donors and acceptors by a virtual electrochemical equilibrium of the form:

$$CO_2(g) + 2Fe^{2+} = CO_2^{2-}(ad) + 2Fe^{3+} \qquad [18]$$

as

$$\Gamma CO_2^{2-} = K pCO_2 (Fe^{2+}/Fe^{3+})^2 \qquad [19]$$

where ΓCO_2^{2-} is a (low) surface concentration and K is a temperature dependent constant for each system. The rate of the dissociation of CO_2 is then proportional to ΓCO_2^{2-}.

All the melts which have been found to fit this model are known to exhibit significant semiconductivity. Ionic current efficiencies during electrolysis at iron saturation have been found to lie between about 2.5 and 90 pct.[19,20,21] Possibly, the class of melts for which expression [17] holds is restricted to those showing relatively high electronic charge mobility. At low iron oxide (or other transition metal oxide) content the rate of charge transfer may be insufficient to maintain the virtual equilibrium represented by Eq. [18]. Other rate determining mechanisms would then be expected to dominate.

ACKNOWLEDGMENTS

The authors acknowledge the support of this work by The Broken Hill Proprietary Company Ltd. One of us, S. S., thanks the Ministry of Education of the People's Republic of China for the provision of a Post-Graduate Fellowship.

REFERENCES

1. Y. Sasaki, S. Hara, D. R. Gaskell, and G. R. Belton: *Metall. Trans. B*, 1984, vol. 15B, pp. 563-71.
2. S. K. El-Rahaiby, Y. Sasaki, D. R. Gaskell, and G. R. Belton: *Metall. Trans. B*, 1986, vol. 17B, pp. 307-16.
3. L. S. Darken and R. W. Gurry: *J. Am. Chem. Soc.*, 1946, vol. 68, pp. 798-816.
4. H. Larson and J. Chipman: *Trans. AIME*, 1953, vol. 197, pp. 1089-96.
5. Y. Takeda, S. Nakazawa, and A. Yazawa: *Can. Met. Quart.*, 1980, vol. 19, pp. 297-305.
6. E. J. Michal and R. Schuhmann, Jr: *Trans. AIME*, 1952, vol. 194, pp. 723-29.
7. M. Timucin and A. E. Morris: *Metall. Trans.*, 1970, vol. 1, pp. 2193-201.
8. S. Ban-ya, A. Chiba, and A. Hikosaka: *Tetsu-to-Hagané*, 1980, vol. 66, pp. 1484-93.
9. S. Hara, T. Araki, and K. Ogino: *Proc. Int. Symp. on Metallurgical Slags and Fluxes*, H. A. Fine and D. R. Gaskell, eds., TMS-AIME, Warrendale, PA, 1984, pp. 441-51.
10. S. Ban-ya, Y. Iguchi, and T. Nagasaka: *Tetsu-to-Hagané*, 1983, vol. 69, p. S761 and 1984, vol. 70, pp. A21-24; also, T. Nagasaka, Y. Igushi, and S. Ban-ya: *Proc. 5th Int. Iron and Steel Congress*, vol. 3, pp. 669-78, Iron and Steel Soc., AIME, Warrendale, PA, 1986.
11. F. Tsukihashi, K. Kato, K. Otsuka, and T. Soma: *Trans. Iron and Steel Inst. Jpn.*, 1982, vol. 22, pp. 688-95.
12. H. A. Fine, D. Meyer, D. Janke, and H-J. Engel: *Ironmaking Steelmaking*, 1985, vol. 12, pp. 157-62.
13. G. R. Belton: *Proc. Int. Symp. on Metallurgical Slags and Fluxes*, H. A. Fine and D. R. Gaskell, eds., TMS-AIME, Warrendale, PA, 1984, pp. 63-85.
14. A. M. Strachan and P. Grieveson: *Metal-Slag-Gas Reactions and Processes*, Z. A. Foroulis and W. W. Smeltzer, eds., The Electrochemical Society, Princeton, NJ, 1975, pp. 38-49.
15. A. W. Cramb, W. R. Graham, and G. R. Belton: *Metall. Trans. B*, 1978, vol. 9B, pp. 623-29.

16. H. W. Melville and B. G. Gowenlock: *Experimental Methods in Gas Reactions*, MacMillan and Co., London, 1964.
17. F. D. Richardson: *Physical Chemistry of Melts in Metallurgy*, Academic Press Inc., London, 1974, vol. 2, p. 331.
18. J. A. Imlach and F. P. Glasser: *Trans. Brit. Ceram. Soc.*, 1973, vol. 72, pp. 221-28.
19. M. T. Simmnad, G. Derge, and I. George: *Trans. AIME*, 1954, vol. 200, pp. 1386-90.
20. W. R. Dickson and E. B. Dismukes: *Trans. TMS-AIME*, 1962, vol. 224, pp. 505-11.
21. E. A. Dancy and G. Derge: *Trans. TMS-AIME*, 1966, vol. 236, pp. 1642-48.